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17C 004244

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1. Your reference

High Efficiency EL DEVICES

2. Patent application number

(The Patent Office will fill in this

9619382.6

17 SEP 1996

3. Full name, address and postcode of the or of each applicant (underline all surnames)

CAMBRIDGE DISPLAY TECHNOLOGY LTD.  
ISIA HUNTER & CO LTD.  
CAMBRIDGE  
CB3 0DS

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

17C 6166441002

4. Title of the invention

High Efficiency EL DEVICES

5. Name of your agent (if you have one)

PAGE WHITE &amp; FARRER

Address for service in the United Kingdom to which all correspondence should be sent (including the postcode)

54 DOUGHTY STREET  
LONDON

WC1N 2LS

Patents ADP number (if you know it)

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Country	Priority application number (if you know it)	Date of filing (day / month / year)
UK	9615883.7	29/07/96

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day / month / year)
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:
- 
- a) any applicant named in part 3 is not an inventor, or
- 
- b) there is an inventor who is not named as an applicant, or
- 
- c) any named applicant is a corporate body.
- 
- See note (d))

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Description	4
Claim(s)	
Abstract	
Drawing(s)	4

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Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination  
(*Patents Form 10/77*)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

13-9-96

12. Name and daytime telephone number of person to contact in the United Kingdom

Dr Paul May  
0223 276351

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## HIGH EFFICIENCY EL DEVICES

### Field:

The field of the invention relates to the construction of organic light emitting diodes.

### Background:

Organic electroluminescent devices are made from materials that emit light when a suitable voltage is applied across electrodes deposited on either side of the polymer. One class of such materials is semiconductive conjugated polymers which have been described in our earlier patent US, 5,247,190, the contents of which are herein incorporated by reference. Poly(p-phenylene vinylene) [PPV], for instance, will emit light when positive and negative charge carriers are passed through the material by applying a voltage between two suitable electrodes. The electroluminescent efficiency of these devices is known to depend on the balancing of the electrons and holes that are injected into the device and meet to form electron/hole pairs, as well as on the efficiency with which these electron/hole pairs combine to radiate light i.e. the photoluminescence efficiency (for example, see N.C. Greenham and R.H. Friend, Solid State Physics, 49, 1, 1995). Therefore it is of critical importance for an efficient device to have sufficiently high photoluminescence efficiency.

There are several approaches used for the processing of conjugated polymers. One approach uses a precursor polymer which is soluble and can therefore be easily coated by standard solution-based processing techniques (for example, spin-coating and blade-coating). The precursor is then converted *in situ* by suitable heat treatment to give the fully conjugated and insoluble polymer. The other approach uses directly soluble conjugated polymers which do not require a subsequent conversion stage. Depending on the specific application, one or other of the approaches might be relevant. The precursor polymer approach can be especially important where subsequent processing might lead to damage of the polymer film if it were directly soluble - such processing may be, for instance, coating with further polymer layers (for example, transport layers or emitting layers of different colour), or patterning of the top electrode. Converted precursor films also have better thermal stability which is of importance both during fabrication but also for the storage and operation of devices at high temperatures.

Where the precursor polymer is converted to the final form by elimination or modification of a solubilising group it is generally important that these by-products of the conversion process are removed from the film. It may also be important that they do not interact with the substrate during this process, for example if this causes harmful impurities to move into the film from the substrate thus affecting the performance (including luminescence efficiency and lifetime) of the electroluminescent device. We have observed, for instance, a quenching of the photoluminescence when precursor PPV polymers are converted on conductive oxide substrates such as indium tin oxide. This, we believe, is caused by indium compounds being released into the PPV due to the reaction of one of the conversion by-products (for example, hydrogen halide) with the indium tin oxide.

In addition, to the observation of quenching via the presence of impurities from the interaction of by-products with indium tin oxide during conversion, we have also observed detrimental effects due to the enhanced conversion of certain PPV copolymers. Such copolymers normally have limited conjugation lengths as compared to the homopolymer case. This normally leads to exciton confinement and therefore high photoluminescence and electroluminescence efficiencies. In this case, we believe, that the indium compounds present in certain PPV copolymer films when converted on indium tin oxide can catalyse the elimination of groups designed to survive the conversion process. The ITO protection layer therefore also provides an effective barrier to prevent this process in this case.

The invention describes a device structure and a method of manufacture for an electroluminescent device that overcomes this problem.

**Invention:**

According to one aspect of the invention there is provided a multilayer electroluminescent device incorporating a converted precursor polymer as the emitting layer and an electrode protecting layer placed between the converted precursor polymer and the underlying electrode and which acts to protect the electrode during the precursor conversion process. At least one other layer is present one of which is the second electrode.

In one embodiment a layer of transparent conducting material deposited on glass or plastic and forms one of the electrodes, typically the anode of the device. Examples of suitable anodes include tin oxide and indium tin oxide. Typical layer thicknesses are 500-2000A and resistivities are 10-100 Ohm/square, and preferably < 30 Ohm /square. The converted precursor polymer can be, for instance, poly(p-phenylene vinylene) [PPV] or a homopolymer or copolymer derivative of PPV. The thickness of this layer can be in the range 500-2000A. The substrate protecting layer is chosen to act as a barrier against the conversion by-products of the precursor polymer, but also must not act as a barrier to the injection of holes from the anode into the emitting layer, where they combine with electrons injected from the cathode to radiate light. Conducting polymers are a general class of materials that can combine ease of processing, protection of the underlying electrode, and suitable hole transporting and injecting properties and are therefore good candidates. Very thin layers (10-500 A) are used and therefore the transparency of the layer can be high. Typical resistivities of these layers are 100-1000 ohm/square. Examples include conjugated polymers that have been doped including polythiophenes, polyanilines, polypyroles, and derivatives thereof. The cathode electrode is placed on the other side of the converted precursor material and completes the device structure. Furthermore, undoped conjugated polymers, as listed above, may also be used where the doping occurs in situ, by interaction with the conversion by-products during device manufacture.

In another embodiment the electrode protection layer and the precursor polymer is deposited on the cathode, typically a material such as aluminium or an alloy of aluminium with a low work function element or any low work function element or alloy. In this case the protection layer will need to transport electrons, but may or may not need to be transparent. Again conducting polymers are suitable candidates as electrode protection layers. The anode electrode is placed on the other side of the converted precursor material and completes the device structure.

In yet another embodiment a protection layer to either the anode or cathode as described above is provided, but where the protection layer is an undoped conjugated polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a soluble PPV derivative or alternatively a precursor PPV or PPV derivative material. In the latter case, because the protection layer is typically much thinner than the electroluminescence layer, the by-products of the conversion process are more easily removed and therefore any interaction with the electrode during conversion is reduced.

In yet another embodiment a protection layer to either the anode or cathode as described above is provided, but where the protection layer is an evaporated, sputtered, or reactively sputtered thin film which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a thin layer of evaporated carbon, a sputtered layer of amorphous silicon or tin oxide, or a sublimed organic semiconductor layer.

In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is an undoped polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example would be polyvinyl carbazole which is a good hole transporting material but is not a conjugated polymer. Alternatively very thin layers of polymer materials which have relatively poor hole and electron mobilities may function as good electrode protectors without compromising the balance of electron and hole

charge carriers. An example would be polystyrene.

In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is a very thin dielectric which provides a barrier to the precursor conversion by-products, but which is thin enough that holes can tunnel through it when it is in contact and protecting the anode or electrons can tunnel through it when it is in contact and protecting the cathode.

In yet another embodiment a protection layer for either the anode or the cathode as described above is provided, but where the protection layer is a sacrificial layer. During the conversion process the sacrificial layer is etched away by the conversion by-products, the subsequent products of this interaction are chosen such that they do not interfere with the photoluminescence or electroluminescence efficiencies of the converted precursor conjugated polymers. Examples of such protection layers would include non-stoichiometric oxide films, such as silicon and aluminium oxides, the layer thickness being determined by the degree of interaction during the conversion process.

A second aspect of the invention provides a method of manufacture of an electroluminescence device wherein a precursor to a conjugated polymer material is deposited on a substrate on which has previously been deposited both an electrode layer and subsequently an electrode protection layer. The precursor is then converted to the final conjugated polymer form before deposition of a subsequent layer or layers at least one of which is the second electrode.

**Drawing:**

Figure 1. Electroluminescent device structure incorporating an electrode protection layer.

Figure 2. Conversion route of a standard PPV precursor.

**Specific Embodiment:**

A specific embodiment is now described. Indium tin oxide is deposited using either dc or rf sputtering techniques onto polished glass substrates. Such substrates are available commercially. Typical products use soda lime glass with a thin silica barrier and an indium tin oxide layer of resistivity of 30 Ohm/square and transparency of about 85%, with a thickness of order 1500A. A polythiophene based conducting polymer system is used as a protection layer - Polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS) - which is available from Bayer AG, Leverkusen, Germany as Trial Product AI 4071. A 100A film of the conducting polymer is spin-coated on the substrate before spin-coating the precursor polymer which is typically a homopolymer PPV developed by us. With this precursor polymer the solubilising group that is removed during conversion is tetrahydrothiophene, and the counter-ion to the thiophene salt is bromine. Another by-product is therefore hydrogen bromide which readily attacks ITO and can cause the release of detrimental products into the film which quenches the photoluminescence. Without the protector layer, the PL efficiency and therefore the EL efficiency of the PPV material is reduced from about 13% to, at best, about 0.7% following the thermal conversion process at 150 °C in nitrogen for 4 hours. However, with the protector layer PL efficiency of ~3% is obtained. After the conversion a suitable cathode material, calcium for instance, is deposited on top of the conjugated polymer. The final device structure is indicated in Figure 1 and the conversion by-products of the PPV-based precursor are indicated in Figure 2. Devices made with the protector layer typically have significantly improved electroluminescence efficiency compared to the devices without the protector layer. Relative photoluminescence efficiencies are detailed in Table 1.

Another specific embodiment is now described. Indium tin oxide is deposited using either dc or rf sputtering techniques onto polished glass substrates. Such substrates are available commercially. Typical products use soda lime glass with a thin silica barrier and an indium tin oxide layer of resistivity of 30 Ohm/square and transparency of about 85%, with a thickness of order 1500A. A polythiophene based conducting polymer system is used as a protection layer - Polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS) - which is available from Bayer AG, Leverkusen, Germany as Trial Product AI 4071. A 100A film of the conducting

polymer is spin-coated on the substrate before spin-coating the precursor polymer which is typically an acetate-based PPV copolymer developed by us. This material has a very high photoluminescence (PL) efficiency, where the solubilising group that is removed during conversion is tetrahydrothiophene, and the counter-ion to the thiophene salt is bromine. Another by-product is therefore hydrogen bromide which readily attacks ITO and can cause the release of detrimental products into the film which quenches the photoluminescence and causes enhanced conversion. Without the protector layer, the PL efficiency and therefore the EL efficiency of the PPV material is dramatically reduced from about 60% to, at best, about 7% following the thermal conversion process - 150C in nitrogen for 4 hours. However, with the protector layer a PL efficiency of ~22% is obtained following conversion. After the conversion a suitable cathode material, calcium for instance, is deposited on top of the conjugated polymer. The final device structure is indicated in Figure 1 and the conversion by-products of the PPV-based precursor are indicated in Figure 2. Devices made with the protector layer typically have significantly improved electroluminescence efficiency compared to the devices without the protector layer. Relative photoluminescence efficiencies are detailed in Table 1. The copolymer referred to in this case contains ~20 mol % of the acetate function. Modification of the copolymer acetate level has led to photoluminescence efficiencies of over 30% when converted on ITO with the PEDT/PSS protection layer. Figures 3 to 5 show that protection of the PPV copolymer is also brought about minimising the enhanced conversion with the ITO protection layer. The UV spectra show little change in the homopolymer case irrespective of the substrate used. However, there is a clear red shift for the acetate based copolymer when converted on ITO. In addition, there is an absorption peak at 1737 cm<sup>-1</sup> in the IR spectra which is assigned to the acetate carbonyl absorption. The relative intensity of this can be compared with other peaks in the spectrum, such as the absorption at 1517cm<sup>-1</sup> which originates in the aromatic constituents of the polymer. The ratio of the intensities of the two peaks therefore gives a measure of the relative quantities of the acetate function. Table 2 shows that this ratio (acetate:aromatic) is significantly reduced when the conversion is carried out on bare ITO. We interpret these results as enhanced conversion of the acetate based copolymer by indium compounds from the ITO substrate and this process is reduced by the presence of ITO protection layers.

FIGURE 1: LEP DEVICE INCORPORATING ITO PROTECTION LAYER

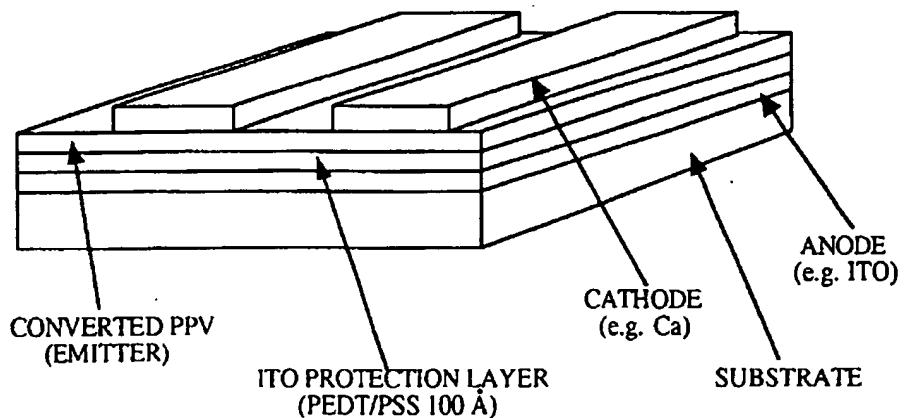


FIGURE 2: PREPARATION OF PPV

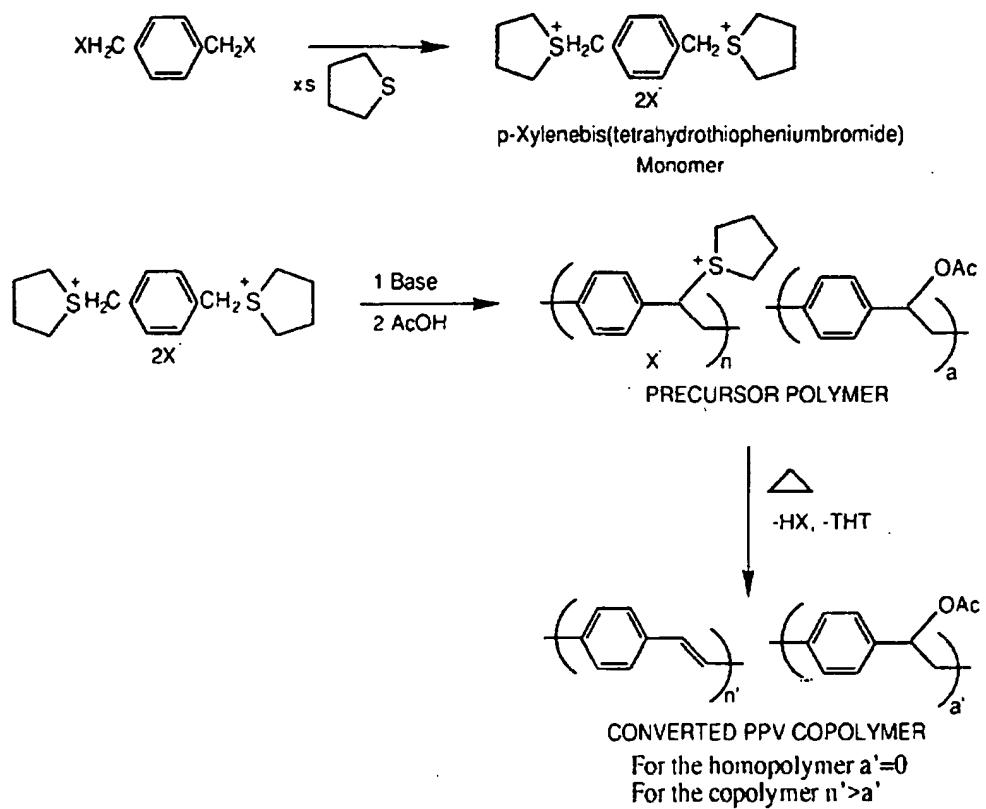


Figure 3: UV Spectra PPV Homopolymer Converted on Quartz, ITO, and ITO/Protection Layer

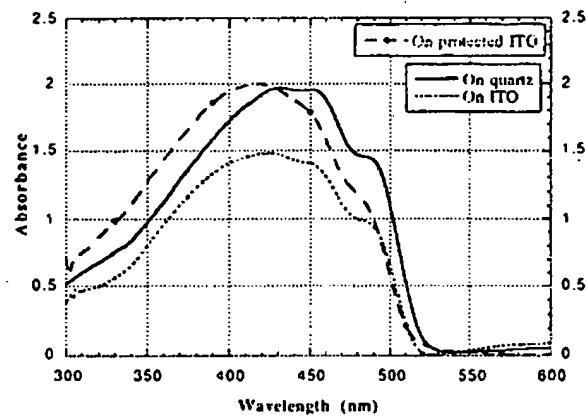
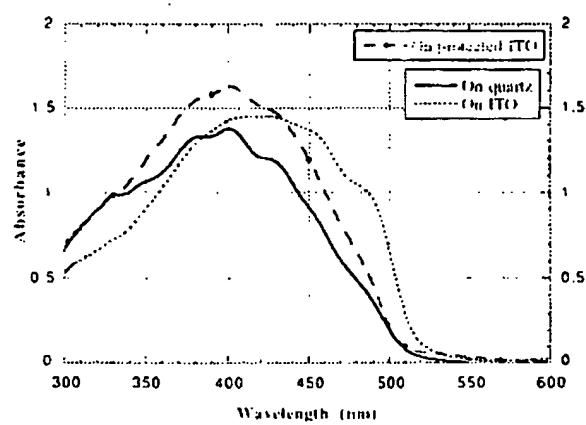


Figure 4: UV Spectra PPV Copolymer Converted on Quartz, ITO, and ITO/Protection Layer



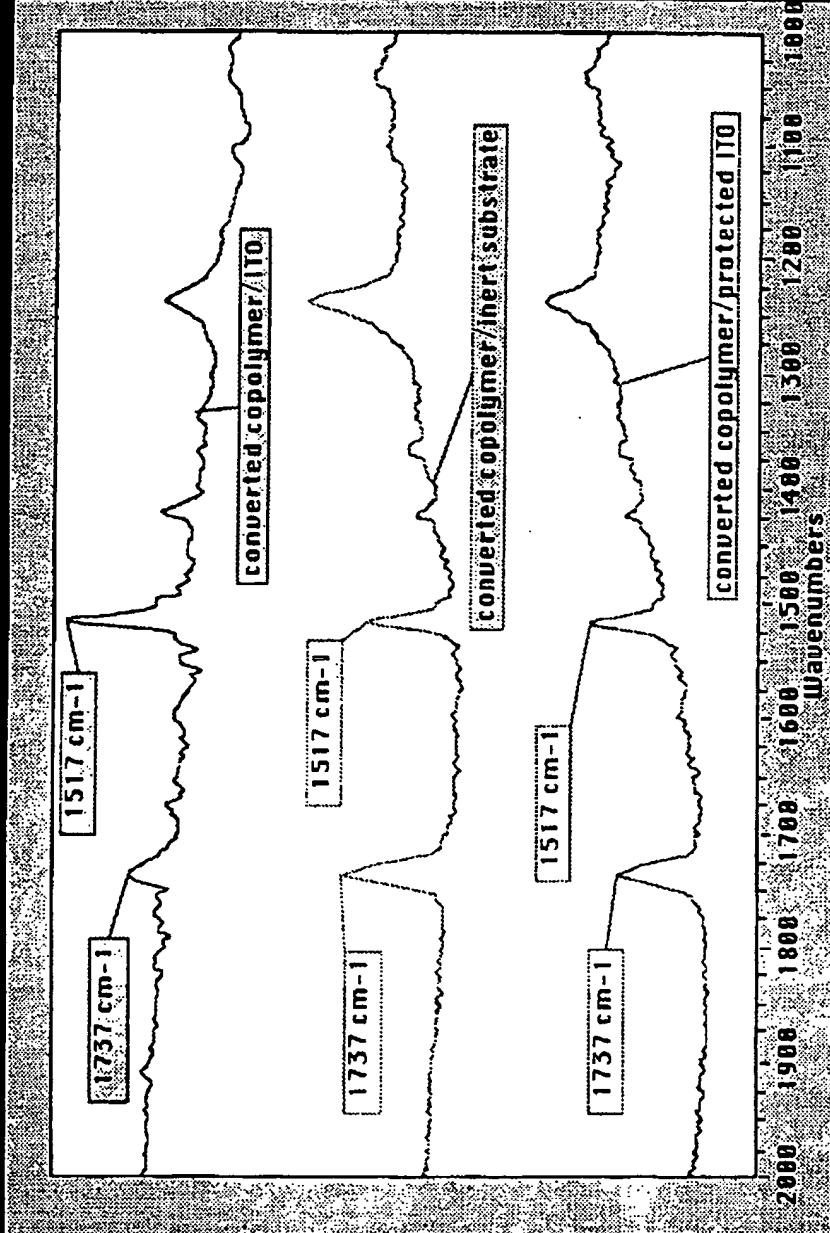


Figure 5: IR Spectra of Acetate Based Copolymer Converted on an inert substrate (Silicon), ITO, and the ITO/Protection Layer

TABLE 1: RELATIVE PHOTOLUMINESCENCE EFFICIENCY (%)  
MEASUREMENTS

Polymer Type	PL eff/Quartz	PL eff/ITO	PL eff/Protection Layer /ITO
Homopolymer	13.2	0.7	3
Copolymer	56	6.8	22

TABLE 2: 1737/1517 cm-1 Ratios (Acetate:Carbonyl) from IR spectra

Substrate	1737/1517 cm-1 Ratio*
Inert(Si)	1.1
ITO/Protection Layer	1
ITO	0.3

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